

## III.A Materials

### III.A.1 SOFC Research and Development

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#### Objectives

- Explore the mechanisms of chromium-related solid oxide fuel cell (SOFC) performance degradation.
- Explain why chromium poisoning appears to be more severe at 700°C than at 800°C.

#### Approach

- Determine and compare cell performance degradations with different interconnect materials and temperatures.
- Measure chrome contents in cathodes from cell tests and in cathodes that were equilibrated in contact with bipolar plate materials.
- Determine weight loss of chrome oxide at different water concentrations in the gas phase.

#### Accomplishments

- SOFC performance degradation due to chromium poisoning of the cathodes was shown to indeed be faster at 700°C than at 800°C.
- Three different mechanisms were identified that can cause chromium poisoning, with oxyhydroxide evolution from the bare metal being responsible for the accelerated effect at 700°C.
- Thermogravimetric analyses have unequivocally shown that weight loss attributed to oxyhydroxide volatility is proportional to the water content in the gas phase.
- Chromium volatility is lower from compounds like  $\text{MnCr}_2\text{O}_4$  or  $\text{LaCrO}_3$ .
- Lanthanum ferrite cathodes were shown to be more severely affected by chromium poisoning than lanthanum manganite.

#### Future Directions

- The reason for the diminished cathode performance will be investigated.
- Methods for diminishing the chromium migration will be explored.
- The nature of the chrome species in the cathode and whether solid-state diffusion is related to the oxide conductivity of the cathode will be explored.

## **Introduction**

Chromium contamination of SOFC cathodes has been observed by several groups of researchers developing stacks with metallic bipolar plates. When a chromium source is present, the cells exhibited significant performance declines, leading to speculation that chromium contamination may “poison” the cathode performance. Hilpert et al. have attributed the chromium transport to the formation of volatile oxyhydroxide species that form when chromium-containing steels are exposed to oxygen and water at elevated temperatures (1, 2). The oxyhydroxide (primarily  $\text{CrO}_2(\text{OH})_2$  (3)) can form either by reaction of the surface oxide with oxygen and water, or by direct reaction of metallic chromium (4), which then deposits at the active cathode sites (5). A good overview of many issues associated with metallic-based interconnects is provided by Quadakkers (6). Other issues being considered are cathode/electrolyte interactions and compositions (7). In addition to vapor-phase transport, because the interconnect is in direct contact with the cathode, chromium may also diffuse into the cathode by a solid-state mechanism. In this report we present the results of work addressing the degradation of cell performance in the presence of different steels, the chemical reactivity of steels with cathode materials and volatilization from various chromium sources.

## **Approach**

The primary approach used to investigate chromium poisoning of the SOFC cathode was to operate SOFC cells at a constant potential of 0.7 volts and observe performance degradation. SOFCs of 2.5 cm X 2.5 cm and similar-sized samples of either 430 SS, EBrite, or Crofer 22 APU were used. Additionally, metal particles of the same alloy were placed on top of the cathode. Next, a Pt mesh current collector was placed on top of the cathode and particles, followed by the metallic plate with slits cut in it. Cells with lanthanum strontium iron oxide (LSF), lanthanum strontium manganese oxide (LSM), or an A-site-deficient LSF were operated at 700°C and 800°C. Air at 2% humidity was used as the cathode gas and hydrogen, with 3% humidity, as the anode gas. The cells were operated until 50% of the initial current was supported at 0.7 volts.

Postoperation analysis was done by scanning electron microscopy (SEM), and Cr distribution was determined by energy dispersive x-ray spectroscopy (EDS).

A second set of experiments examined the weight loss of  $\text{Cr}_2\text{O}_3$ ,  $\text{MnCr}_2\text{O}_4$  and  $\text{LaCrO}_3$  by thermogravimetric analysis. Alumina was used as a standard to correct for any buoyancy effects. Runs were carried out at 700°C and 800°C using 3 mol% or 25 mol%  $\text{H}_2\text{O}$  in a carrier gas of 20%  $\text{O}_2$  in Ar, with a flow rate of 50 sccm. The materials were allowed one hour to equilibrate with respect to environment prior to data collection.

## **Results**

Results of the cell tests are shown in Figures 1a and 1b. Figure 1a shows polarization curves of a cell with an LSM cathode and a 430 SS interconnect at 700°C after 2, 48, 144, 168, and 216 hours of operation. The polarization curve declines quite rapidly, and after 200 hours only half the initial current was sustained. Figure 1b shows the cell current at 0.7 V versus the operation time at 800°C and at 700°C. While the cell current at 700°C was significantly smaller than at 800°C, consistent with a higher resistance at lower temperatures, both cells show a significant decrease in current. However, the decline at 700°C appears more rapid than at 800°C, implying increased poisoning at lower temperature.

Similar results were observed with both EBrite and Crofer 22 APU materials. SEM was used to examine the degraded cells, with EDS used to determine the chromium content through the cathode. Figure 2 provides SEM images, Figure 3 the corresponding chromium profiles, of the cross section of three cells with different cathodes, all tested with Crofer 22 APU. An LSM cathode, Figure 2a, had very little chromium after 200 hours, while the different LSF cathodes, Figures 2b and 2c, had much higher chromium after 50 hours, with the heavily A-site-deficient LSF having the highest chromium content.

### *Thermogravimetric Analysis*

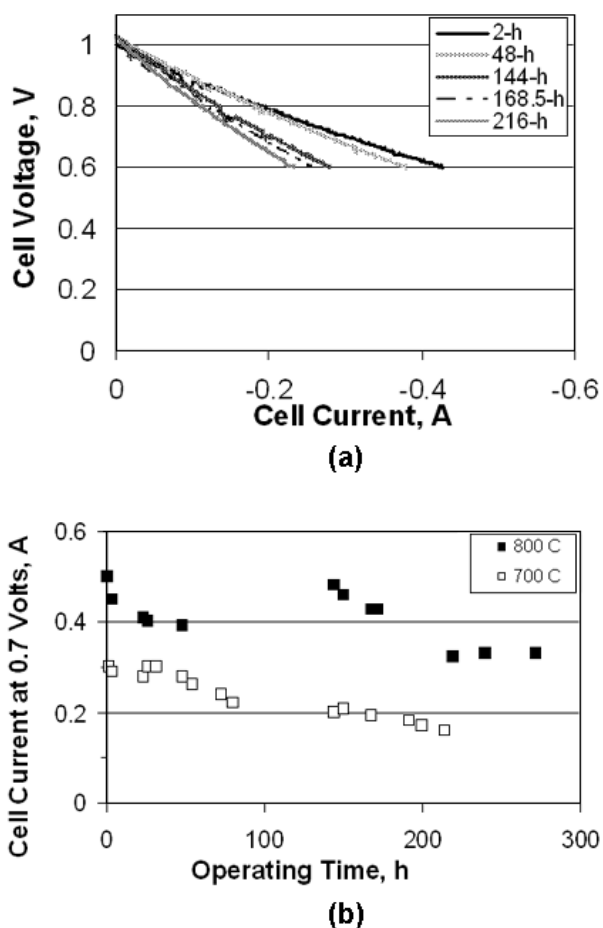
Shown in Figure 4 are the mass losses from chromia powder measured by thermogravimetric analysis in flowing air at 700°C and 800°C with either

3 or 25% water in the air. Chromia clearly reacts with oxygen and water to form a volatile species, and based on thermodynamic analysis this should be primarily  $\text{CrO}_2(\text{OH})_2$ . The material loss is on the order of micrograms per hour and shows dependence on both temperature and water content of air.

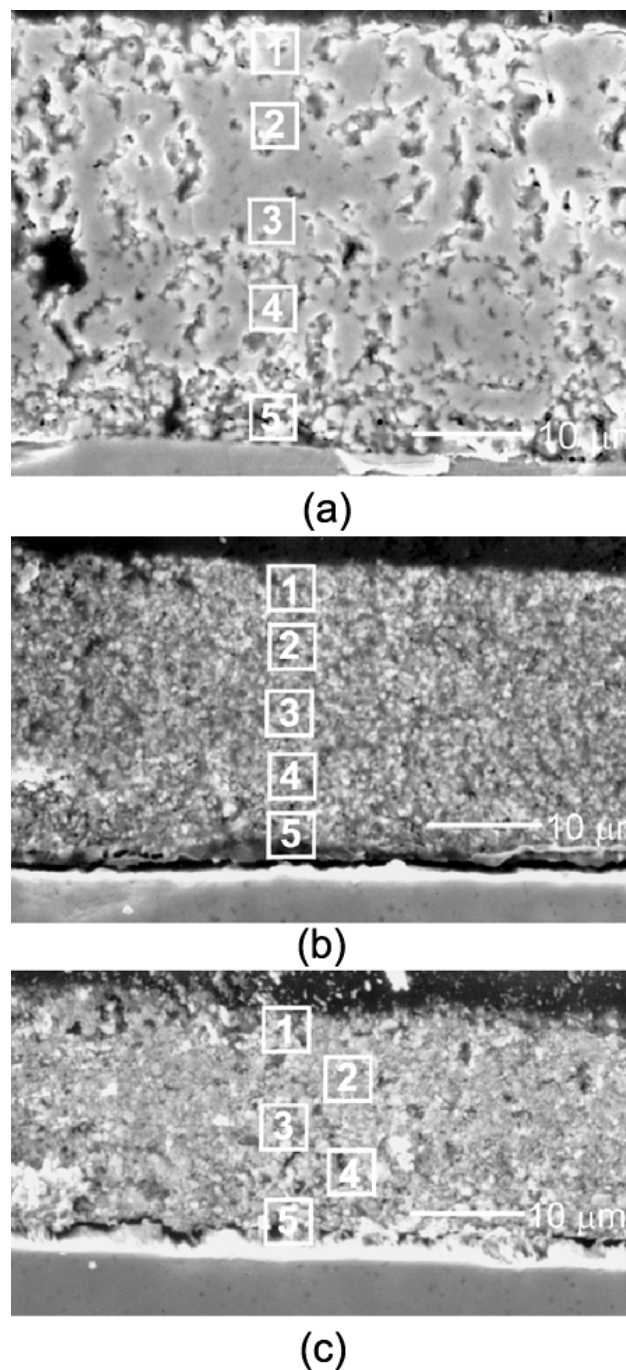
### Discussion

Having examined the issue of chromium poisoning from several different perspectives, it appears that no single mechanism may be completely responsible for the interactions between stainless steel and SOFC cathodes. The volatile oxyhydroxide species can form by a reaction of air and steam with

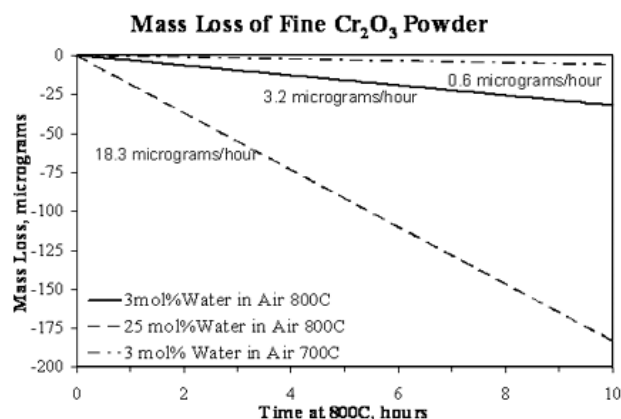
the bare metal or with the protective chromium oxide layer. The reaction with the metal is thermodynamically favored and appears to be faster. Poisoning of cathodes is more rapid at 700°C because the interconnect surface is essentially bare. At



**Figure 1.** (a) Polarization Curves of InDec Cell #17 with LSM and 430 SS at 700°C and 2% Humid Air, Showing Ongoing Performance Decline, and (b) Cell Current at 0.7 V for Two SOFCs with LSM Cathode, 430 SS and Humid 2% Air, One at 700°C and the Other at 800°C



**Figure 2.** SEM of (a) LSM Cathode, (b) LSF Cathode, and (c) A-site-deficient LSF Operated at 800°C with a Crofer 22 APU Interconnect



**Figure 4.** Comparison of the Mass Loss from Chromia under Various Conditions; the Species of Mass Loss is Expected to be  $\text{CrO}_2(\text{OH})_2$

800°C, the metal surface oxidizes to form a protective oxide scale, which is less reactive with oxygen and steam.

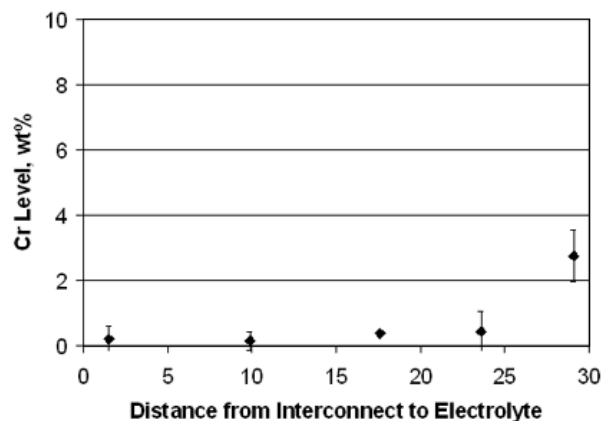
However, solid-state diffusion also seems to play a role in the migration of chromium. In both the cell tests and the solid-state equilibrations, the chromium levels were highest in the sub-stoichiometric LSF, followed by stoichiometric LSF and LSM. It is well known that the oxide ion conductivity decreases in that order. Since oxide ion conductivity will not affect the gas-phase diffusion, migration must be by a surface mechanism.

## Conclusions

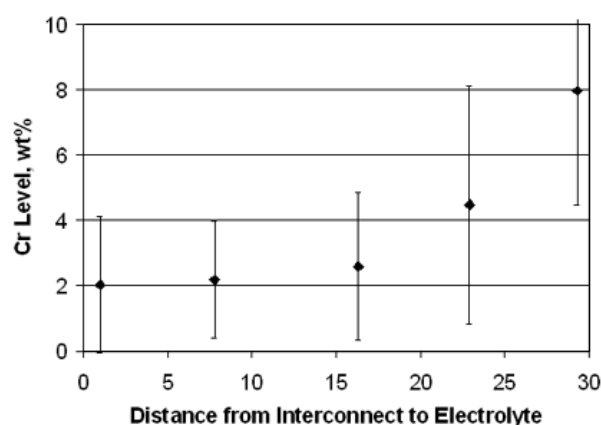
While ferritic stainless-steel-based interconnects are potentially attractive for planar SOFCs, it appears that interactions/reactions involving chromium in either the alloy or the protective scale can interact with the cathode materials. Therefore, the surface of any metallic interconnects will need to either be chromium-free or have chromium in a more stable form, such as a spinel or perovskite phase. However, the long-term relative stability of such materials has not yet been sufficiently examined.

## References

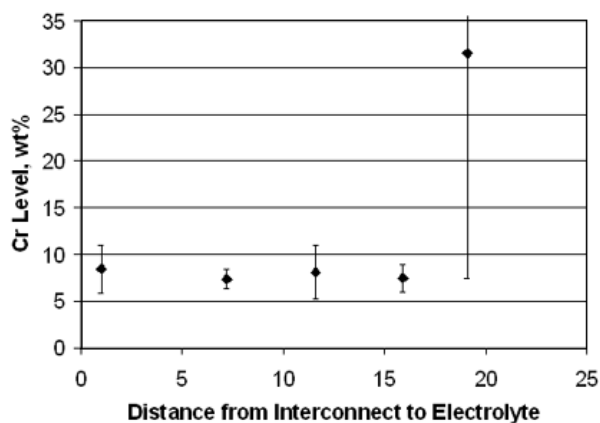
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(a)



(b)



(c)

**Figure 3.** Charts Corresponding to the Chromium Content Determined by EDS for Points 1 through 5 for Each Cathode

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